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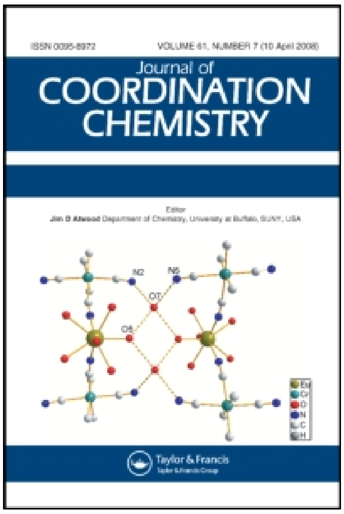

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

COMPLEXES OF BINUCLEATING LIGANDS. VII. SOME COPPER(II) COMPLEXES OF TWO SULPHUR-CONTAINING LIGANDS

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To cite this Article McFadyen, W. D. and Robson, R.(1976) 'COMPLEXES OF BINUCLEATING LIGANDS. VII. SOME COPPER(II) COMPLEXES OF TWO SULPHUR-CONTAINING LIGANDS', Journal of Coordination Chemistry, 5: 2, 49 — 53

To link to this Article: DOI: 10.1080/00958977608075920

URL: http://dx.doi.org/10.1080/00958977608075920

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J. Coord. Chem.
1976, vol. 5, pp. 49–53

COMPLEXES OF BINUCLEATING LIGANDS. VII. SOME COPPER(II) COMPLEXES OF TWO SULPHUR-CONTAINING LIGANDS

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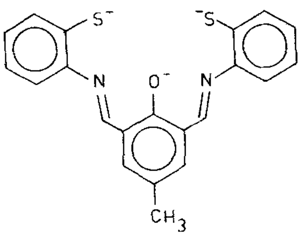
(Received January 3, 1975; in final form May 23, 1975)

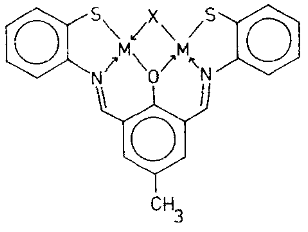
The following cupric complexes of the new binucleating ligand 2-hydroxy-5-methylisophthalaldehyde di-2′-methylmercaptoanil, (hereafter MeLH, the ligand strictly being the derived anion MeL^-) and of the related trianionic ligand (hereafter L^{3-}) formally derived from 2-hydroxy-5-methylisophthalaldehyde di-2′-mercaptoanil have been isolated and characterized:– $Cu_2(MeL)Cl_3$, $Cu_2(MeL)Br_3$, $Cu_3(MeL)Br_5$, $Cu_2(MeL)(OH)(ClO_4)_2$, $Cu_2(L)Cl \cdot DMSO$, $Cu_2(L)(NCO)$, $Cu_2(L)(tz)$ (where tz^- is the anion of 1,2,4-triazole (tzH)). Magnetic properties are consistent with binuclear arrangements in all cases except $Cu_3(MeL)Br_5$.

INTRODUCTION

Recently we reported an extensive series of binuclear Cu(II) and Ni(II) complexes of the trianionic di-Schiff base ligand, I (hereafter L^{3-}), formally derived from 2-hydroxy-5-methyliso-phthalaldehyde di-2′-mercaptoanil[1]. The complexes appear to adopt the basic structure II, where $X^- = OH^-$, $\frac{1}{2}O^{2-}$, RO^-, RS^-, NH_2^-, NHR^-, NR^{2-}, $C_3H_3N_2^-$ (i.e. the pyrazolate anion), and N_3^- and this has been unambiguously demonstrated by X-ray crystallography in the case X^- = pyrazolate[2]. A matter of some concern to us in the initial survey of the range of species which could be incorporated at the exchangeable bridging site was the fact that we were unable to isolate complexes II with $X^- = Cl^-$,[1] despite the common occurrence of chloro-bridged species. Alternative approaches to the desired chloro-bridged species were therefore sought.

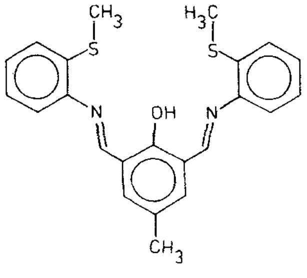


I



II

A route to thiol complexes[3], of particular convenience in some cases where the thiol is not easily accessible[4], is provided by S-dealkylation of the related coordinated thioether. In the hope of employing this approach to obtain the desired chloro-bridged complexes of L^{3-} we have synthesised the new binulceating ligand 2-hydroxy-5-methyliso-phthalaldehyde di-2′-methylmercaptoanil, III (hereafter MeLH). Although these expectations were not realised a number of complexes of MeL^- were isolated and identified and these, together with some new complexes of L^{3-}, are described herein.



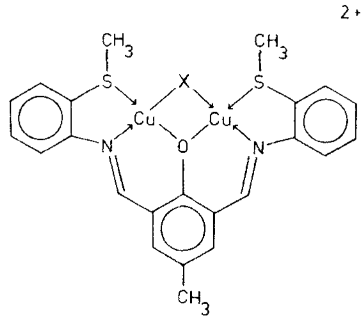
III

RESULTS AND DISCUSSION

Orange crystalline MeLH, prepared by condensation of 2-methylthioaniline with 2-hydroxy-5-methylisophthalaldehyde in acetonitrile, was characterised by elemental analysis and by its ir and mass spectrum. In the ir spectrum the aldehydic C = 0 st. of the starting material at 1680 cm^{-1} is absent, and the strong new band at 1620 cm^{-1} is tentatively assigned to the C = N st. The mass spectrum of MeLH shows a molecular ion peak, M^+, at m/e 406 (10%, M^+ theor. 406) and the base peak at m/e 391 corresponds to loss of methyl radical from the molecular ion.

The crystalline complexes $Cu_2(MeL)Cl_3$, $Cu_2(MeL)Br_3$, $Cu_3(MeL)Br_5$ and $Cu_2(MeL)(OH)(ClO_4)_2$ were obtained as indicated in the Experimental Section.

The structures of $Cu_2(MeL)Cl_3$, $Cu_2(MeL)Br_3$ and $Cu_2(MeL)(OH)(ClO_4)_2$ are very likely based upon the anticipated binuclear unit, IV, where $X^- = Cl^-$, Br^- or OH^- respectively, although we do not intend to suggest that such units are necessarily isolated in the crystal as discrete dications eg. Cu coordination numbers may well be higher than 4. Support for the presence of binuclear units is provided by magnetic data, whilst the fact that the ir spectra of the complexes are virtually identical (apart from bands associated with ClO_4^- in $Cu_2(MeL)(OH)(ClO_4)_2$) is consistent with the idea that they are closely related structurally. The complex $Cu_2(MeL)(OH)(ClO_4)_2$ is diamagnetic, and the experimental magnetic data for $Cu_2(MeL)Cl_3$ and $Cu_2(MeL)Br_3$ could be fitted to molar susceptibility values calculated from the Bleaney-Bowers equation[5] using $2J = -208\ \mathrm{cm}^{-1}$, $g = 2.03$ and $N\alpha = 60\ \mathrm{cm}^3\ \mathrm{mol}^{-1}$ for $Cu_2(MeL)Cl_3$ and $2J = -195\ \mathrm{cm}^{-1}$, $g = 2.03$ and $N\alpha = 80\ \mathrm{cm}^3\ \mathrm{mol}^{-1}$ for $Cu_2(MeL)Br_3$. The agreement between the calculated and experimental susceptibility values is shown in Figure 1. Diamagnetic binuclear Cu(II) complexes are not without precedent; for example, the hydroxo bridged Cu(II) complexes of related binucleating ligands[1,6] are effectively diamagnetic.



IV

A number of modes can readily be envisaged for the association between the basic binuclear unit $[Cu_2(MeL)(X)]^{2+}$ and the counter ions, the details of which cannot be determined with certainty from the

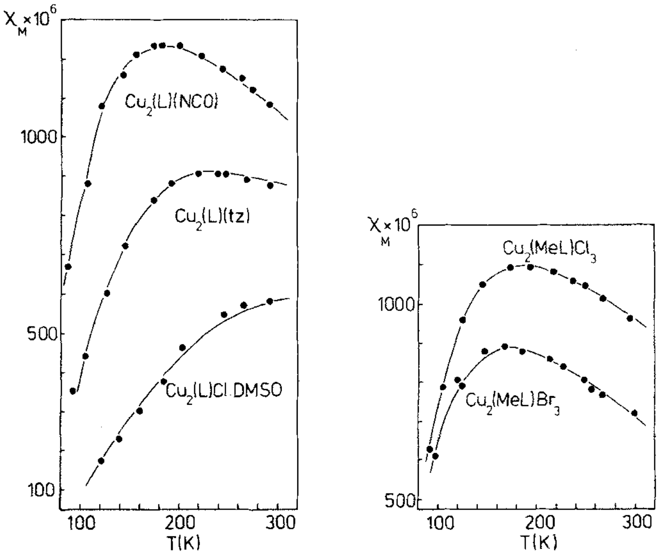


FIGURE 1 Plots of molar susceptibility per cupric ion, χ_M, versus temperature. Calculated curves (————), experimental points (●). The theoretical curve and experimental points for $Cu_2(MeL)Br_3$ are lowered 300 cx $10^6\ \mathrm{cm}^3\ \mathrm{mol}^{-1}$ to avoid confusion in the figure.

evidence available. However, in the case of $Cu_2(MeL)(OH)(ClO_4)_2$ the ir spectrum (ClO_4^- bands (nujol, cm^{-1}) occur at 1080 (broad, strong), 932 (sharp, weak) and 625 (sharp, strong)) indicates that the perchlorate ions are uncoordinated[7,8] and that $[Cu_2(MeL)(OH))]^{2+}$ exists as a discrete cation in the solid. The magnetic properties of the chloride and bromide are also consistent with a magnetically isolated binuclear cation. Electronic spectra are of no use in this connection being dominated by charge transfer bands which obscure any $d \leftrightarrow d$ transitions (the complexes are brown). A broad and weak band at 3460 cm^{-1} in the ir spectrum (nujol mull)of $Cu_2(MeL)(OH)(ClO_4)_2$ is associated with the bridging hydroxo group.

Since it is possible that the metal atoms in the complexes may not be equivalent it might seem that the Bleaney-Bowers equation[5] (which was originally derived for the $Cu(OAc)_2 \cdot H_2O$ system in which the metal centres are equivalent) is not an adequate model for such systems. However, this is not the case as has been shown recently by application of Griffith's General Theory of Magnetic Susceptibility[9] to the general case of a Cu(II) dimer[10].

The magnetic data of $Cu_3(MeL)Br_5$ (Table I) cannot be fitted to the Bleaney-Bowers equation although the basic binuclear unit $[Cu_2(MeL)Br]^{2+}$ is probably present since the infra-red spectra of $Cu_2(MeL)Br_3$ and $Cu_3(MeL)Br_5$ are virtually identical. However, $Cu_3(MeL)Br_5$ cannot consist of discrete $[Cu_2(MeL)Br]^{2+}$ cations and $CuBr_4^{2-}$ anions because even if the cation were diamagnetic the $CuBr_4^{2-}$ would produce a paramagnetic susceptibility[11] at low temperature far in excess of that observed. Although the exact structural arrangement of $Cu_3(MeL)Br_5$ cannot be assigned on the basis of the evidence presently available, a lattice consisting essentially of equal numbers of $[Cu_2(MeL)Br]^{2+}$ units and $CuBr_4^{2-}$ units with some degree of bridging between these species via the bromide components of $CuBr_4^{2-}$ appears very reasonable.

In our earlier work[1] L^{3-} complexes were generally obtained by reaction between the appropriate metal carboxylate and sources of both the bridging species and L^{3-} (a benzothiazoline[1], which we shall hereafter refer to as $B(LH_3)$), or by exchange of one bridging group for another. Attempts to produce $Ni_2(L)X$, $X = Cl^-, Br^-, I^-$, employing the former method led to the separation of $[Ni_2(L)]_2[O]$[1], whereas halo containing complexes of unacceptable purity resulted from similar efforts with copper(II). Efforts to exchange the bridging groups of any of the established complexes of the type $M_2(L)X$[1] ($M = Cu^{II}, Ni^{II}$) with halide ions were unsuccessful, and either the starting complex was recovered unchanged or decomposed in a manner unaffected by the presence of halide ions.

Recently, however, we have been able to obtain $Cu_2(L)Cl \cdot DMSO$ by gently warming a suspension of $Cu_2(L)(N_3)$[1] in a solution of copper(II) chloride in DMSO. Gas evolution occurred and an intense brown solution resulted which on cooling deposited crystalline $Cu_2(L)Cl \cdot DMSO$. The course of this reaction is surprising when it is considered that $Cu_2(L)(N_3)$ may be recovered unchanged after prolonged heating, in a variety of solvents, with either excess Et_4NCl or various Cu(II) salts (apart from the halides). In addition, we have isolated two new Cu(II) complexes of L^{3-}, viz., $Cu_2(L)(NCO)$ and $Cu_2(L)(tz)$, where tz^- is the anion of 1,2,4-triazole (tzH).

Each of $Cu_2(L)Cl \cdot DMSO$, $Cu_2(L)(NCO)$ and $Cu_2(L)(tz)$ very likely adopts the structure depicted by II. Their ir spectra show the same basic pattern displayed by the other L^{3-} complexes[1], and the magnetic data of all three can be "fitted" to the Bleaney-Bowers equation[5] using $2J = -387$ cm^{-1}, $g = 2.04$ and $N\alpha = 35$ cm^3 mol^{-1} for $Cu_2(L)Cl \cdot DMSO$; $2J = -200$ cm^{-1}, $g - 2.15$ and $N\alpha = 30$ cm^3 mol^{-1} for $Cu_2(L)(NCO)$; and $2J = -262$ cm^{-1}, $g = 2.11$ and $N\alpha = 20$ cm^3 mol^{-1} for $Cu_2(L)(tz)$. The agreement between the experimental and calculated susceptibility values is shown in Figure 1.

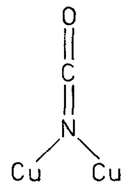
By analogy with the case of $Cu_2(L)(N_3)$ the bridging mode of the cyanato anion is very likely as in V. When the cyanato group bridges terminally,

TABLE I
Magnetic Data of $Cu_3(MeL)Br_5$

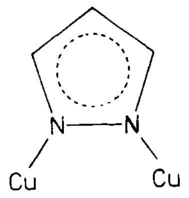
T(K)	288	268	245	218	189	174	145	123	103	92
$\chi_M \times 10^6$ cm^3 mol^{-1}	694	706	722	736	719	692	646	604	553	480
μ_{eff} BM†	1.26	1.23	1.19	1.13	1.04	0.98	0.87	0.77	0.67	0.59

†Calculated from $\mu_{eff} = 2.828\sqrt{\chi_M} \cdot T$

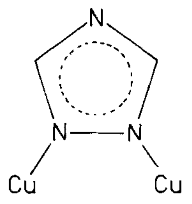
bonding is usually considered to be through the N atom[12,13], as established in the case of the binary cyanate $AgNCO$[14]. It has been recently established by crystallography[2] that the pyrazolate anion in $Cu_2(L)(pz)$ bridges the Cu(II) ions as shown by VI. In view of the structural similarities between tz^- and pz^- it is likely that the tz^- anion in $Cu_2(L)(tz)$ bridges in a like manner as in VII.



V



VI



VII

EXPERIMENTAL

Unless otherwise stated, materials were dried at 80°C in vacuum.

2-hydroxy-5-methylisophthalaldehyde

The dialdehyde 2-hydroxy-5-methylisophthalaldehyde was prepared by the method of Ullman and Brittner[15]. m.p. (uncorrected) 132–133°C, Lit. 133.5°C[15].

2-hydroxy-5-methylisophthalaldehyde di-2'-methylmercaptoanil, MeLH

A hot solution of 2-hydroxy-5-methylisophthalaldehyde (2g) in acetonitrile (40 ml) was added to a hot solution of 2-methylthioaniline (20 ml) in acetonitrile (20 ml) to give a red solution which on stirring and cooling deposited the product as pale orange crystals. The produce was collected and washed with diethyl ether. m.p. (uncorrected) 161.3°C. Anal. Calcd. for $C_{23}H_{22}N_2S_2O$: C, 67.8; H, 5.4; N, 6.9; S, 15.8; O, 3.9. Found: C, 67.7; H, 5.3; N, 7.0; S, 15.7; O, 4.2.

2-methylthioaniline

This was prepared by methylation of 2-aminothiophenol (Koch-light, technical grade) following the method of Livingstone[16].

4-hydroxy-3, 5-bis[2'-benzothiazolinyl] toluene, B(LH B(LH_3)

This was prepared as previously reported[1].

MeL^- Complexes

$Cu_2(MeL)Cl_3$ A hot solution of MeLH (1g) in DMSO (16 ml) was added to a solution of cupric chloride dihydrate (2.52 g) in ethanol (200 ml) at the boiling point. Almost immediately the resultant brown solution deposited glistening brown crystals of $Cu_2(Me)Cl_3$. After the reaction mixture had cooled the product was collected and washed with ethanol and then diethyl ether.

Anal. Calcd. for $C_{23}H_{21}N_2S_2OCl_3Cu_2$: C, 43.2; H, 3.3; N, 4.4; S, 10.0; Cl, 16.6; Cu, 19.9. Found: C, 43.3; H, 3.3; N, 4.3; S, 9.8; Cl, 16.7; Cu, 19.7.

$Cu_2(MeL)Br_3$ A hot solution of MeLH (0.80 g) in DMSO (16 ml) was added to a solution of cupric bromide (3.66 g) and lithium acetate monohydrate (0.20 g) in ethanol (200 ml) at the boiling point. Almost immediately the resultant intense brown solution deposited fine brown crystals of $Cu_2(MeL)Br_3$. After the reaction mixture had cooled the product was collected and washed with ethanol and then diethyl ether. Anal: Calcd. for $C_{23}H_{21}N_2S_2OBr_3Cu_2$: C, 35.8; H, 2.7; N, 3.6; S, 8.3; Br, 31.1; Cu, 16.4. Found: C, 35.8; H, 2.8; N, 3.5; S, 8.2; Br, 31.0; Cu, 16.4.

$Cu_3(MeL)Br_5$ This was prepared using the same quantities as for $Cu_2(MeL)Br_3$, except that the lithium acetate monohydrate was omitted. When the cupric bromide and MeLH solutions were mixed, $Cu_2(MeL)Br_3$ separated almost immediately. The resulting suspension was held at the boiling point for two hours during which time the $Cu_2(MeL)Br_3$ was replaced by darker and finer crystals of $Cu_3(MeL)Br_5$. The product was collected from the hot suspension and washed with ethanol. Anal. Calcd. for $C_{23}H_{21}N_2S_2OBr_5Cu_3$: C, 27.7; H, 2.1; N, 2.8; S, 6.4; Br, 40.2; Cu 19.2. Found: C, 27.4; H, 2.0; N, 2.7; S, 6.6; Br, 40.2; Cu, 18.9.

$Cu_2(MeL)(OH)(ClO_4)_2$ A boiling solution of hexaaquo copper(II) perchlorate (5.48 g) and lithium acetate monohydrate (0.40 g) in methanol (240 ml) was added to solid MeLH (0.80 g) and the reaction mixture was boiled until the MeLH had dissolved. The resultant brown-green solution was quickly filtered and then maintained at the boiling point for about five minutes, during which time glistening brown-black crystals of $Cu_2(MeL)(OH)(ClO_4)_2$ separated. The product was collected from the hot suspension, washed with methanol and then dried in vacuum. Anal. Calcd. for $C_{23}H_{22}N_2S_2O_{10}Cl_2Cu_2$:

C, 36.8; H, 3.0; N, 3.7; S, 8.6; Cl, 9.5; Cu, 17.0. Found: C, 36.8; H, 3.5; N, 3.5; S, 8.3; Cl, 9.3; Cu, 16.6.

L^{3-} Complexes

$Cu_2(L)Cl \cdot DMSO$ A solution of cupric chloride dihydrate (0.76 g) in DMSO (18 ml) was added to solid $Cu_2(L)(N_3)$[1] (0.6 g). Upon gently warming and stirring, the suspended $Cu_2(L)(N_3)$ dissolved, accompanied by gas evolution, to yield an intense brown solution, which then deposited fine brown crystals. After the reaction mixture had cooled the product was collected, washed with DMSO, and then dried in vacuum. Anal. Calcd. for $C_{23}H_{21}N_2O_2S_3Cu_2Cl$: C, 44.8; H, 3.4; N, 4.5; S, 15.6; Cu, 20.6; Cl, 5.8. Found: C, 44.5; H, 3.6; N, 4.8; S, 16.0; Cu, 20.4; Cl, 5.6.

$Cu_2(L)(tz)$ A hot solution of 1,2,4-triazole (0.51 g) in DMF (50 ml) was added to a suspension of $Cu_2(L)(OC_2H_5)$[1] (1 g) in DMF (100 ml). Upon warming and stirring, an intense brown solution resulted, which on cooling deposited fine brown crystals. The product was collected, and washed with DMF and then diethyl ether. Anal. Calcd. for $C_{23}H_{17}N_5OS_2Cu_2$: C, 48.4; H, 3.0; N, 12.3; S, 11.2; Cu, 22.3. Found: C, 48.8; H, 3.2; N, 12.5; S, 10.9; Cu, 22.0.

$Cu_2(L)(NCO)$ A hot solution of $B(LH_3)$ (1 g) in DMSO (20 ml) was added to a hot solution of cupric acetate monohydrate (0.87 g), $Cu(DMSO)_5(OH_2)(ClO_4)_2$ (4.60 g) and sodium cyanate (1.50 g), all in DMSO (60 ml). The resultant intense brown solution deposited fine brown needles on cooling, and these were collected and washed with DMSO and then acetone. This material corresponded to $Cu_2(L)(NCO) \cdot nDMSO$, in which the DMSO content varied from preparation to preparation, but was usually close to 1. The solvated material was then taken and gently boiled in acetone (200 ml), when it was replaced by smaller brown crystals of the DMSO free product. This material was collected and washed with acetone. Anal. Calcd. for $C_{22}H_{15}N_3O_2S_2Cu_2$: C, 48.5; H, 2.8; N, 7.7; S, 11.7; Cu, 23.3. Found: C, 48.6; H, 2.7; N, 7.7; S, 11.4; Cu, 23.4.

$Cu(DMSO)_5(OH_2)(ClO_4)_2$ This was prepared as described by Fee et al[17].

Physical Methods and Instrumentation

Infra-red spectra were recorded using a Perkin-Elmer 421 Spectrophotometer. Samples were mounted in KBr discs and/or nujol or hexachlorobutadiene mulls between KBr plates.

Diffuse reflectance spectra were recorded by use of a Beckman DK-2A Spectrophotometer.

Mass spectra were recorded on an A.E.I. MS9 high resolution Mass Spectrometer operating at 70 eV.

Magnetic susceptibilities were determined by the Gouy method using freshly prepared $Hg[Co(NCS)_4]$ as calibrant.

Analyses were performed by the Australian Microanalytical Service at the University of Melbourne.

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